

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/EP04/013249

International filing date: 19 November 2004 (19.11.2004)

Document type: Certified copy of priority document

Document details: Country/Office: EP
Number: 03079123.0
Filing date: 19 December 2003 (19.12.2003)

Date of receipt at the International Bureau: 18 January 2005 (18.01.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

03079123.0

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk





Anmeldung Nr:
Application no.: 03079123.0
Demande no:

Anmelde tag:
Date of filing: 19.12.03
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

UNILEVER N.V.
Weena 455
3013 AL Rotterdam
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Detergent granules and process for their manufacture

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

C11D/

Am Anmelde tag benannte Vertragstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL
PT RO SE SI SK TR LI



19. 12. 2003

C7739-ff

(90)

DETERGENT GRANULES AND PROCESS FOR THEIR MANUFACTURE

TECHNICAL FIELD

5

The present invention relates to granulated detergent compositions comprising an encapsulated perfume.

BACKGROUND OF THE INVENTION

10

It is known to incorporate perfumes into granulated detergent compositions, in the form of so-called "microcapsules". One known form of microcapsule consists of melamine-urea-formaldehyde microcapsules having a perfume core. Modern high bulk density detergent granules are conventionally prepared by mechanical mixing and densification of the surfactant and other components (usually including detergency builder) either to form the final product or to prepare a pre-granulated concentrated adjunct to which one or more other ingredients may be post-dosed. However, to incorporate perfume microcapsules into the material being agglomerated in this way has been found to result in various negatives, such as poor dispersibility, with subsequent mechanical loss, undesirable residues and product inefficacy (from the point of view of delivery of the perfume).

20

Dry addition of the microcapsules tends to result in loose agglomerates of the capsules which are then difficult to disperse throughout the composition without use of significant shear forces, resulting in subsequent noticeable perfume loss.

Another alternative route of dropping the microcapsules onto the rest of the composition on a conveyer also tends to result in undesirable cluster formation.

25

This problem has now been solved by incorporating the encapsulated perfume in a slurry and spraying the slurry onto a powdered (preferably pre-granulated) composition which comprises one or more conventional ingredients of detergent compositions. This results in so-called "layered" detergent granules which comprise a functional core of the conventional detergent ingredient(s) and an outer layer comprising the encapsulated perfume.

35

The so-called "layering" of detergent granules is well-known in the art, usually in the context of adding a "layering agent" (usually, an aluminosilicate) in the final stage of non-spray drying mechanical granulating process for detergents, for example as
5 described in "Surfactants in Consumer Products", Springer Verlag, 1987, pp 411-413. This is usually done to improve the flow properties of the product and/or to control granule size distribution during the agglomeration process.

DEFINITION OF THE INVENTION

10

A first aspect of the present invention provides a granulate detergent product comprising coated granules which comprise a functional core which comprises one or more deterutive agents selected from surfactants and dergency builders, the coated granules further comprising up to 10% by weight of a coating which comprises
15 encapsulated perfume.

A second aspect of the present invention provides a granulate detergent product in which at least 10% of the total number of granules are coated granules which comprise a functional core which comprises one or more deterutive agents selected from
20 surfactants and dergency builders, the coating comprising encapsulated perfume.

A third aspect of the present invention provides a process for making a granulate detergent product, the process comprising:-

25

- (i) providing a powdered and/or granulated deterutive composition comprising one or more deterutive agents selected from surfactants and/or dergency builders;
- (ii) preparing a slurry comprising water and an encapsulated perfume;
- (iii) spraying the deterutive composition with said slurry to form coated
30 granules.

The resultant product of this process may, for example, fulfil the requirements of the first and/or second aspect of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In the process of the present invention, the slurry is applied in an amount such that the coating on the granules constitutes up to 10% by weight of those granules. However,

- 5 preferably, the coated particles constitute up to 5%, more preferably up to 3%, 2.5% or 2%, still more preferably up to 1% by weight or even up to 0.75% or 0.5% by weight of the coating.

- In the case of the second aspect of the invention, the coated granules constitute at 10 least 10% but preferably at least 15%, 20%, 25%, 30%, 35%, 40%, 45% or 50%, eg at least 80% or 90% of the number of granules.

- It is also preferred to incorporate some non-encapsulated perfume in the slurry, 15 preferably in an amount of from 0.0001% to 50%, more preferably from 25% to 50% by weight of the slurry, or preferably in a weight ratio of unencapsulated perfume to the perfume capsules of from 1:10 to 1:1, more preferably from 1:2 to 1:1.

- Other ways of incorporating unencapsulated perfume are to blend the coated granules with perfume or to spray it on to those finished granules, before or simultaneously with 20 application of the slurry.

Preferably also, a viscosity modifier in the form of a lubricant such as glycerol is included in the slurry to facilitate pumping and atomisation.

- 25 Preferably, the $d_{3,2}$ average particle diameter of the coated detergent granules is from 180 μm to 1,400 μm , more preferably from 500 μm to 710 μm .

The Encapsulated Perfume

- 30 A number of different encapsulated perfumes suitable for use in detergent compositions are commercially available. A preferred kind of such capsule is in the form of melamine-urea-formaldehyde microcapsules, available from 3M Corporation or BASF.

The encapsulated perfume is preferably dispersed in the slurry (which comprises water) in an amount of from 5% to 80%, more preferably from 40% to 80% by weight of the slurry.

5 The Granulation Apparatus

A process according to the second aspect of the present invention may be carried out in either batch or continuous mode of operation as desired.

- 10 The process of the invention is preferably carried out in a mechanical granulator, most preferably a low- or moderate shear machine. A low- or moderate-shear mixer/granulator often has a stirring action and/or a cutting action which are operated independently of one another. Preferred types of low- or moderate-shear mixer granulators are mixers of the Fukae^R FS-G series; Diosna^R V series ex Dierks &
15 Sohne, Germany; Pharma Matrix^R ex. T.K. Fielder Ltd, England. Other mixers which are suitable for use in the process of the invention are Fuji^R VG-C series ex Fuji Sangyo Co., Japan; the Roto^R ex Zanchetta & Co. srl, Italy and Schugi^R Flexomix granulator.
- 20 Another possible low shear granulator is one of the gas fluidisation type, which comprises a fluidisation zone in which the liquid binder is sprayed into or onto the solid neutralising agent. However, a low shear bowl mixer/granulator can also be used. When the low shear granulator is of the gas fluidisation kind it may sometimes be preferable to use equipment of the kind provided with a vibrating bed. This may be
25 preferable if the perfume loading of the slurry is to be low and when drying is required. Gentle heating of the fluidisation air is preferred to avoid premature perfume release.

If the low-shear granulator is of the gas fluidisation kind, then the liquid binder can be sprayed from above and/or below and/or within the midst of the fluidised material.

- 30 If a gas fluidisation granulator is used as the low-shear granulator, then preferably it is operated at a superficial air velocity of about $0.1\text{-}2.0 \text{ ms}^{-1}$, either under positive or negative relative pressure and with an air inlet temperature ranging from -10° or 5°C up to 80°C , or in some cases, up to 200°C . An operational temperature inside the bed of from ambient temperature to 60°C is typical. Depending on the process, it may be
35

advantageous to vary the temperature (upwardly and/or downwards, during at least part of the process).

Compositional Features

5

The core of the granulate granules made by a process according to the present invention contains at least one surfactant and/or detergency builder. Any such ingredient may also additionally be incorporated in the coating, via the slurry.

- 10 In addition, any granulate according to the present invention may be incorporated in a detergent composition comprising one or more post dosed materials. Optionally, any granulate or detergent composition according to any aspect of the present invention may be compressed into tablet form by known technique, eg such a tablet also comprising a disintegrant. Such a tablet constitutes a further aspect of the invention.

15

Surfactants

- Suitable surfactants are selected from one or more of anionic, non-ionic, cationic, zwitterionic and ampholytic surfactants. In general, suitable surfactants include those generally described in "Surface active agents and detergents" Vol. I by Schwartz and Perry. If desired, soap derived from saturated or unsaturated fatty acids having, for example, C₁₀ to C₁₈ carbon atoms may also be present.

- Anionic surfactant may actually comprise one or more different anionic surfactant compounds. Preferred anionic surfactants are alkylbenzene sulphonates, particularly so-called linear alkylbenzene sulphonates having an alkyl chain length of C₈-C₁₅. It is preferred if the level of linear alkylbenzene sulphonate is from 0 wt% to 30 wt%, more preferably 1 wt% to 25 wt%, most preferably from 2 wt% to 15 wt%.

- 30 The granulates of the invention may additionally or alternatively contain other anionic surfactants in amounts additional to the percentages quoted above. Suitable anionic surfactants are well-known to those skilled in the art. Examples include primary and secondary alkyl sulphates, particularly C₈-C₁₅ primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

The granulates of the invention may also contain non-ionic surfactant. Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C₈-C₂₀ aliphatic alcohols ethoxylated with an average of from 1 to 20

- 5 moles of ethylene oxide per mole of alcohol, and more especially the C₁₀-C₁₅ primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).
- 10 It is preferred if the level of non-ionic surfactant is from 0 wt% to 30 wt%, preferably from 1 wt% to 25 wt%, most preferably from 2 wt% to 15 wt%.

Detergency Builders

- 15 Preferred detergency builders are alkali metal, preferably sodium, aluminosilicate builder. Sodium aluminosilicates may generally be incorporated in amounts of from 10 to 70% by weight (anhydrous basis), preferably from 25 to 50 wt%.

- 20 The alkali metal aluminosilicate may be either crystalline or amorphous or mixtures thereof, having the general formula: 0.8-1.5 Na₂O. Al₂O₃. 0.8-6 SiO₂

- 25 These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO₂ units (in the formula above). Both the amorphous and the crystalline materials can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature. Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1 429 143 (Procter & Gamble). The preferred sodium aluminosilicates of this type are the well-known commercially available zeolites A and X, and mixtures thereof.

- 30 The zeolite may be the commercially available zeolite 4A now widely used in laundry detergent powders. However, according to a preferred embodiment of the invention, the zeolite builder incorporated in the compositions of the invention is maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP 384 070A (Unilever). Zeolite MAP is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to

aluminium ratio not exceeding 1.33, preferably within the range of from 0.90 to 1.33, and more preferably within the range of from 0.90 to 1.20.

Especially preferred is zeolite MAP having a silicon to aluminium ratio not exceeding

- 5 1.07, more preferably about 1.00. The calcium binding capacity of zeolite MAP is generally at least 150 mg CaO per g of anhydrous material.

Organic builders that may be present include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphinates; monomeric 10 polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di and trisuccinates, carboxymethoxy succinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts. This list is not intended to be exhaustive.

- 15 Especially preferred organic builders are citrates, suitably used in amounts of from 5 to 30 wt%, preferably from 10 to 25 wt%; and acrylic polymers, more especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, preferably from 1 to 10 wt%.

- 20 Builders, both inorganic and organic, are preferably present in alkali metal salt, especially sodium salt, form.

Other Optional Ingredients

- 25 Granulates according to any aspect of the present invention may also contain one or more other ingredients such as bleaches and/or bleach systems, enzymes, dyes, anti-dye transfer agents, dye fixatives, fluorescers, antigooms etc. These may be incorporated in the core, but optionally, may additionally or alternatively be introduced via the slurry to be incorporated in the core.

- 30 Thus, granulates according to the invention may also suitably contain a bleach system. Fabric washing compositions may desirably contain peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, capable of yielding hydrogen peroxide in aqueous solution.

Suitable peroxy bleach compounds include organic peroxides such as urea peroxide, and inorganic persalts such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates. Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate.

5

Especially preferred is sodium percarbonate having a protective coating against destabilisation by moisture. Sodium percarbonate having a protective coating comprising sodium metaborate and sodium silicate is disclosed in GB 2 123 044B (Kao).

- 10 The peroxy bleach compound is suitably present in an amount of from 0.1 to 35 wt%, preferably from 0.5 to 25 wt%. The peroxy bleach compound may be used in conjunction with a bleach activator (bleach precursor) to improve bleaching action at low wash temperatures. The bleach precursor is suitably present in an amount of from 0.1 to 8 wt%, preferably from 0.5 to 5 wt%.

15

Preferred bleach precursors are peroxycarboxylic acid precursors, more especially peracetic acid precursors and peroanoic acid precursors. Especially preferred bleach precursors suitable for use in the present invention are N,N,N',N'-tetracetyl ethylenediamine (TAED) and sodium nonanoyloxybenzene sulphonate (SNOBS). The 20 novel quaternary ammonium and phosphonium bleach precursors disclosed in US 4 751 015 and US 4 818 426 (Lever Brothers Company) and EP 402 971A (Unilever), and the cationic bleach precursors disclosed in EP 284 292A and EP 303 520A (Kao) are also of interest.

- 25 The bleach system can be either supplemented with or replaced by a peroxyacid. Examples of such peracids can be found in US 4 686 063 and US 5 397 501 (Unilever). A preferred example is the imido peroxycarboxylic class of peracids described in EP A 325 288, EP A 349 940, DE 382 3172 and EP 325 289. A particularly preferred example is phthalimido peroxy caproic acid (PAP). Such peracids are suitably present at 0.1 - 30 12%, preferably 0.5 - 10%.

A bleach stabiliser (transition metal sequestrant) may also be present. Suitable bleach stabilisers include ethylenediamine tetra-acetate (EDTA), the polyphosphonates such as Dequest (Trade Mark) and non-phosphate stabilisers such as EDDS (ethylene diamine

di-succinic acid). These bleach stabilisers are also useful for stain removal especially in products containing low levels of bleaching species or no bleaching species.

An especially preferred bleach system comprises a peroxy bleach compound (preferably sodium percarbonate optionally together with a bleach activator), and a transition metal bleach catalyst as described and claimed in EP 458 397A, EP 458 398A and EP 509 787A (Unilever).

The granulates according to the invention may also contain one or more enzyme(s).

Suitable enzymes include the proteases, amylases, cellulases, oxidases, peroxidases and lipases usable for incorporation in detergent compositions. Preferred proteolytic enzymes (proteases) are, catalytically active protein materials which degrade or alter protein types of stains when present as in fabric stains in a hydrolysis reaction. They may be of any suitable origin, such as vegetable, animal, bacterial or yeast origin.

Proteolytic enzymes or proteases of various qualities and origins and having activity in various pH ranges of from 4-12 are available and can be used in the instant invention. Examples of suitable proteolytic enzymes are the subtilisins which are obtained from particular strains of B. Subtilis B. licheniformis, such as the commercially available subtilisins Maxatase (Trade Mark), as supplied by Genencor International N.V., Delft, Holland, and Alcalase (Trade Mark), as supplied by Novozymes Industri A/S, Copenhagen, Denmark.

Particularly suitable is a protease obtained from a strain of *Bacillus* having maximum activity throughout the pH range of 8-12, being commercially available, e.g. from Novozymes Industri A/S under the registered trade-names Esperase (Trade Mark) and Savinase (Trade-Mark). The preparation of these and analogous enzymes is described in GB 1 243 785. Other commercial proteases are Kazusase (Trade Mark obtainable from Showa-Denko of Japan), Optimase (Trade Mark from Miles Kali-Chemie, Hannover, West Germany), and Superase (Trade Mark obtainable from Pfizer of U.S.A.).

Detergency enzymes are commonly employed in granular form in amounts of from about 0.1 to about 3.0 wt%. However, any suitable physical form of enzyme may be used.

The granulates of the invention may also contain alkali metal, preferably sodium carbonate, in order to increase detergency and ease processing. Sodium carbonate may suitably be present in amounts ranging from 1 to 60 wt%, preferably from 2 to 40 wt%. However, compositions containing little or no sodium carbonate are also within
5 the scope of the invention.

Granules of the present invention suitably have a low bulk density in the range 400 to 900 g/l, or 500 to 800 g/l, for example, in the proximity of 650 g/l.

10 The composition may also comprise a post-dosed particulate filler which suitably comprises an inorganic salt, for example sodium sulphate and sodium chloride. The filler may be present at a level of 5 to 60% by weight of the composition.

15 A fully formulated detergent composition incorporating granules produced according to the invention might for example comprise the detergent active and builder and optionally one or more of a flow aid, a filler and other minor ingredients such as colour, perfume, fluorescer, bleaches and enzymes.

The invention will now be illustrated by the following non-limiting examples.

20

EXAMPLES

A drum is fed with detergent powder having the formulation given in the Table below, onto which a slurry of perfume capsules is applied by spraying with a nozzle.

25

Spray system: Eminent E13 spray gun

Nozzle spec: 20 HTE nozzle.

Mixer: standard concrete mixer.

Mixing time: 15 minutes.

30 Batch size: 20kg.

Spray-on rate: 0.8 kg hr⁻¹

Capsule concentration in slurry: 50wt% (balance: water)

Ingredient	Amount (wt%)
SodiumLAS	11.1
NI 7EO	8.6
Soap	2.5
Zeolite A24	26.4
Sokalan CP5 (Polyacrylate)	2.1
SodiumCarbonate	17.6
NaSilicate	2.0
SCMC	0.3
NaSulphate	22.3
Moisture	7.1
Total	100

- 5 Optionally, antifoam, bleach (TAED/percarbonate blend), and proteolytic + lipolytic enzymes are post-dosed.



**CLAIMS**

1. A granulate detergent product comprising coated granules which comprise a functional core which comprises one or more deterutive agents selected from surfactants and detergency builders, the coated granules further comprising up to 10% by weight of a coating which comprises encapsulated perfume.
2. A granulate detergent product according to claim 1, wherein the coating comprises up to 5%, more preferably up to 2%, still more preferably up to 1%, by weight of the coating.
3. A granulate detergent product according to either preceding claim, wherein the coating further comprises unencapsulated perfume.
4. A granulate detergent product according to any preceding claim, wherein the encapsulated perfume comprises melamine-urea-formaldehyde microcapsules.
5. A detergent composition comprising a granulate detergent product according to any preceding claim in admixture with one or more other solid ingredients.
6. A granulate detergent product in which at least 10% of the total number of granules are coated granules which comprise a functional core which comprises one or more deterutive agents selected from surfactants and detergency builders, the coating comprising encapsulated perfume.
7. A process for making a granulate detergent product, the process comprising:-
 - (i) providing a powdered and/or granulated deterutive composition comprising one or more deterutive agents selected from surfactants and/or detergency builders;
 - (ii) preparing a slurry comprising water and an encapsulated perfume;
 - (iii) spraying the deterutive composition with said slurry to form coated granules.

8. A process according to claim 7, wherein the slurry further comprises unencapsulated perfume.
9. A process according to claim 7 or claim 8, wherein the slurry further comprises
5 a viscosity modifier.
10. A process according to any of claims 7 to 9, wherein the slurry is sprayed onto the detergative composition in a low shear mixer or a moderate shear mixer.
- 10 11. A process of preparing a detergent composition, the process comprising preparing coated granules by a process according to any of claims 6 – 9 and admixing the coated granules with one or more other solid ingredients.
12. A process according to any of claims 7 to 11, wherein the coated granules are
15 granules according to any of claims 1 to 5.
13. A process according to any of claims 7 – 11, wherein the coated granules are granules according to claim 6.

19. 12. 2003

C7739-ff(V)

14

**ABSTRACT:****DETERGENT GRANULES AND PROCESS FOR THEIR MANUFACTURE**

- 5 A granulate detergent product comprising coated granules which comprise a functional core which comprises one or more detergents selected from surfactants and detergency builders, the coated granules further comprising up to 10% by weight of a coating which comprises encapsulated perfume.

